

Appendix 2
Review of Registrant Proposed Field Adjustment Factors

A. Methyl Bromide

Stangellhini (2006a) proposes field adjustment factors for methyl bromide based on laboratory and field studies of various application methods. Under Stangellhini's scheme, a field adjustment factor of 100% is assumed for all commodity and space fumigations. This is reasonable because nearly all applied methyl bromide from these applications are eventually released to the atmosphere. However, Stangellhini's soil application method groupings are inconsistent with those developed in DPR's analysis of 47 field methyl bromide studies (Segawa et al., 2000). We derive field adjustment factor estimates taking into consideration data cited in Stangellhini (2006a) and DPR's extensive methyl bromide data set of field studies. The field adjustment factors so derived are consistent with the DPR methyl bromide regulations.

1. Review of the Consortium of Methyl Bromide Registrants proposed adjustments

Stangellhini's (2006a) proposed field adjustment factors are based on a single soil column study (Gan et al., 1997) that is summarized in Yates et al. (1996a):

Shallow injection (6-15in.), bed or broadcast, no tarp, field adjustment factor = 82%
Shallow injection (6-15in.), bed or broadcast, LDPE tarp, field adjustment factor = 82%
Shallow injection (6-15in.), bed or broadcast, HDPE tarp, field adjustment factor = 43%
Deep injection (20+in.), bed or broadcast, no tarp, field adjustment factor = 38%
Deep injection (20+in.), bed or broadcast, LDPE tarp, field adjustment factor = 38%
Deep injection (20+in.), bed or broadcast, HDPE tarp, field adjustment factor = 26%

Where:

LDPE = Low Density Polyethylene Film Tarp

HDPE = High Density Polyethylene Film Tarp.

The Gan et al. study (1997) included documented analytical methods for bromide ion and methyl bromide, frequent sampling and mass balance recoveries near 100%.

Consequently the study is acceptable in terms of data quality. However, with the exception of 30 cm injection depth, the results are single realizations of each test system, thus the results are unreplicated. In addition, such column studies are highly controlled and do not reflect the variability in emissions typical of field applications.

1. DPR Methyl Bromide Soil Application Data Set

Stangellhini's (2006a) application method groupings are inconsistent with DPR's analysis of the methyl bromide field studies in the DPR database for two reasons: 1) the DPR database shows that bed application methods, regardless of the type of tarp used, show very high 24 hour emission values and mass loss (81%), and 2) no significant effect on the highest 24 hour emissions due to depth of injection could be detected. Barry (1999) presents details of the analysis and supports a substantially different structure for

application method groupings where bed and broadcast represent one level of classification, and “tarp” and “no tarp” application methods are a second level of classification. No classification based on depth is included because no differences due to depth of injection were observed in the highest 24-hour flux. While in concept there should be a depth effect, it is likely in practice that application-to-application variability at the field level is too large to detect that effect.

DPR’s data set includes 31 field studies of the application methods consistent with those described by Stangellhini. The mean peak 24-hour emissions from these studies are similar in magnitude as emissions over the entire loss period (approximately 2 weeks) described by Stangellhini (2006a). The DPR mean peak 24-hour emissions (emission ratios) are shown below:

HDPE tarp/broadcast 24-hr emissions (emission ratio) = 24%	(n=13, CV = 52%)
No tarp/broadcast 24-hr emissions (emission ratio) = 37%	(n = 8, CV = 47%)
HDPE tarp/bed 24-hr emissions (emission ratio) = 81%	(n = 9, CV = 38%)

In all cases the first 24 hours following application showed the highest 24-hour emission ratio. Since these emissions are for only the first 24 hours and are similar in magnitude to the Stangellhini (2006a) proposed field adjustment factors, these results indicate that it is likely the Stangellhini (2006a) field adjustment factors are too small.

2. Methyl Bromide Literature Reported Emissions

Methyl bromide data potentially appropriate for developing adjustment factors are found in 5 journal articles: Majewski et al. (1995), Gan et al. (1996), Yates et al. (1996b), Yates et al. (1996c), and Gan et al. (1997). These articles report either direct flux (emission) measurements (e.g. aerodynamic method) in the field or soil column results. No flux chamber estimates of emissions are used at this time because there are significant technical issues associated with flux chamber estimates including: (1) potentially significant effects on the local environmental conditions where the chambers are placed relative to the field as a whole. This effect may be largest for static chambers but may also affect dynamic chambers, (2) the sensitivity of dynamic chamber results to pressure gradients created by the air flow, and (3) the very limited coverage of the field by the sample chambers which can introduce a high degree of heterogeneity in the flux results (Reichman and Rolston, 2002; Majewski et al., 1995; Yates 2006).

Table 1 summarizes the studies cited above and shows emission estimates for Broadcast Tarp and Broadcast Non-tarp methods. Shallow and deep injections are pooled within these two categories per the lack of significant difference associated with injection depth observed in the DPR data set. The mean emission for Broadcast Tarp application method is 40%. The mean emission for Broadcast Non-tarp application method is 66%.

3. Methyl Bromide Field Adjustment Factor Development

The mean peak 24-hour emissions (emission ratios) for the three groups in the DPR methyl bromide regulations are used as the basis for the DPR field adjustment factors. Majewski et al. (1995) conclude that about 50% of the total mass loss occurs in the first 24 hours for both tarp and non-tarp applications. Thus, the well-characterized DPR regulatory emission ratios for Broadcast HDPE Tarp, Broadcast Non-tarp, and Bed Tarp can be reasonably doubled to provide an estimate of the field adjustment factor. Due to the large initial emission ratio for Bed Tarp, 100% loss should be assumed. This results in the following estimates:

Broadcast Tarp = 48%

Broadcast Non-tarp = 74%

Bed Tarp = 100%

Comparison of these DPR emission estimates with the mean mass loss estimates in Table 1 indicates that these DPR database derived estimates are within the variation observed in the literature values. Use of the DPR database derived field adjustment factors is consistent with the methyl bromide regulations and permit conditions.

The Stangellhini (2006a) proposed generalized adjustment function is reasonable and can be implemented to adjust methyl bromide VOC emissions. However, the grouping structure and field adjustment factors proposed for soil applications are not consistent with the structure supported by analysis of the studies in the DPR methyl bromide data set. Thus, the grouping structure has been changed to reflect the actual differences in emissions that were detectable in the DPR data set. Emission of 100% of mass applied for all applications not made to soil is reasonable.

The adjustment for both 1990 and 2004 will need to account for fumigations that were likely made to beds. Those application records should assume 100% of the mass applied is lost. Consistent with the Stangellhini (2006a) proposal, the 1990/91 base year adjustment for soil applications not made to beds should assume the non-tarp mass loss of 74%. This assumption will account for the very permeable LDPE tarps that were in use at the time.

B. Chloropicrin

The document “Analysis of Chloropicrin emissions in the San Joaquin Valley in 1990 and 2004” (Stangellhini, 2006b) proposes to adjust chloropicrin VOC emission estimates for soil applications according to the proportion of applied mass lost observed in field studies of various soil application methods. Emission of 100% of mass applied is assumed for all applications not made to soil. The conceptual basis for this proposal is sound. However, two of the studies used in the Stangellhini (2006b) proposal, Gillis and Smith (2002) and Lee et al. (1994), are not of sufficient quality to be included in the estimation of the adjustment factors. The proposed DPR field adjustment factors use only data judged acceptable by DPR.

1. Review of the Chloropicrin Manufacturers Task Force proposed adjustments

The chloropicrin field adjustment factors proposed by Stangellhini (2006b) are:

Shallow injection (6-15in.), broadcast, no tarp = 62%
Shallow injection (6-15in.), broadcast, LDPE tarp = 62%
Shallow injection (6-15in.), broadcast, HDPE tarp = 37%
Deep injection (20+in.), broadcast, no tarp = 62%
Deep injection (20+in.), broadcast, LDPE tarp = 62%
Deep injection (20+in.), broadcast, HDPE tarp = 37%
Drip-application, surface or buried, HDPE tarp = 9%

Where:

LDPE = Low Density Polyethylene Film Tarp

HDPE = High Density Polyethylene Film Tarp.

2. Chloropicrin Literature Reported Emissions

Gao and Trout (2007) used flux chambers to estimate emissions for several chloropicrin and 1,3-D application methods, including HDPE tarp, HDPE tarp with pre-irrigation, single watering-in, intermittent watering-in, and virtually impermeable film (VIF). Those researchers reported problems maintaining a seal between the soil and the chamber. Due to these problems the chamber methodology results may not accurately measure emissions under field conditions. No flux chamber estimates of emissions are used at this time because there are significant technical issues associated with flux chamber estimates including: (1) potentially significant effects on the local environmental conditions where the chambers are placed relative to the field as a whole. This effect may be largest for static chambers but may also affect dynamic chambers, (2) the sensitivity of dynamic chamber results to pressure gradients created by the air flow, and (3) the very limited coverage of the field by the sample chambers which can introduce a high degree of heterogeneity in the flux results (Reichman and Rolston, 2002; Majewski et al., 1995; Yates 2006). Predictions of chloropicrin emission reductions due to intermittent watering-in methods are subject to considerable uncertainty due to problems noted in Gao and Trout (2007). However, the reductions observed for chloropicrin are qualitatively consistent with demonstrated reductions in MITC emissions for intermittent watering-in methods.

3. Chloropicrin Field Adjustment Factor Development

The Stangellhini (2006b) proposed generalized adjustment function is reasonable and can be implemented to adjust chloropicrin VOC emissions. However, the grouping structure and field adjustment factors proposed for soil application methods are not consistent with that proposed by DPR.

The Beard et al. (1996) study will be used exclusively to produce the DPR field adjustment factors for the shank application method. The emissions from Beard et al. (1996) are shown in Table 2. Similar to the proposed methyl bromide factors, the proposed chloropicrin factors only distinguish between tarp and no tarp. No depth factor will be included. All broadcast tarp method mass loss results will be combined to produce a mean estimate. Emission of 100% of mass applied for all applications not made to soil is reasonable.

The chloropicrin data set is small and, thus, it is impossible to reliably distinguish between emissions for bed and broadcast applications. Thus, no separate field adjustment factor for bed methods will be estimated. Instead, based on the known high emission characteristics of methyl bromide bed applications (Barry, 1999), the chloropicrin emission estimates for bed will be combined with the no tarp method.

The drip/tarp application method is separated because the emissions appear to be substantially lower than the shank methods. Three studies are available to derive a drip tarp adjustment factor: Knuteson and Dolder (2000), Rotonardo (2004), and van Wesenbeeck and Phillips (2000).

The Stangellhini (2006b) proposal argues that tarps used in 1990 were LDPE tarps and were highly permeable, thus the No Tarp loss rate was assigned to the LDPE applications. This assumption is reasonable.

Based upon the proportional reduction observed for MITC, DPR will assume that reduction in chloropicrin emissions for intermittent watering-in is approximately one-third of an untarped application. Other application methods that appear to reduce chloropicrin emissions, such as pre-irrigation and VIF may be problematic due to labeling requirements and other factors (Gao and Trout, 2007). Therefore, these application methods are not recommended at this time.

The mean field adjustment factor of each group will be used as the DPR estimated field adjustment factor value. Results are shown below:

Broadcast/No tarp & Bed field adjustment factor = 64%	(n = 3, CV = 6%)
Broadcast/Tarp field adjustment factor = 44%	(n = 3, CV = 35%)
Broadcast/Tarp with intermittent watering-in = 20%	
Drip/High permeability tarp field adjustment factor = 12.3	(n = 1, CV = N/A)
Drip/Low permeability tarp field adjustment factor = 11.8%	(n = 2, CV = 27%)

The CV values for these chloropicrin groups are smaller than those observed for methyl bromide. However, this data set is substantially smaller.

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Table 1. Summary of methyl bromide mass loss estimates from the literature.

Broadcast Tarp						
Reference	Study Type	Soil Type	Depth (cm)	Mass Loss (%)	Mean (%)	CV (%)
JEQ Vol 24:742	Field	Silty Clay Loam	25	32	40	35
JEQ Vol 25:185	Field	Sandy Loam	25	63		
JEQ Vol 26:310	Column	Sandy Loam	30	43		
JEQ Vol 26:310	Column	Sandy Loam	30	37		
JEQ Vol 26:310	Column	Sandy Loam	60	26		
Broadcast Non-tarp						
Reference	Study Type		Depth (cm)	Mass Loss (%)	Mean (%)	CV (%)
JEQ Vol 24:742	Field	Silty Clay Loam	25	89	66	34
JEQ Vol 26:310	Column	Sandy Loam	20	82		
JEQ Vol 26:310	Column	Sandy Loam	30	71		
JEQ Vol 26:310	Column	Sandy Loam	60	38		
ES&T Vol 30:1629	Column	Sandy Loam	30	77		
ES&T Vol 30:1629	Column	Loamy Sand	30	77		
ES&T Vol 30:1629	Column	Clay	30	37		

Table 2. Mass loss (% of applied mass) for various chloropicrin application methods.

Reference	Application Method	Location	Emissions (%)	Average (%)	CV (%)
Beard (1996)	Broadcast/No Tarp	Arizona	62.5	64.2	6.0
Beard (1996)	Broadcast/No Tarp	Arizona	61.4		
Beard (1996)	Bed/Tarp	Arizona	68.6	44.2	35.6
Beard (1996)	Broadcast/Tarp	Arizona	62.3		
Beard (1996)	Broadcast/Tarp	Washington	33.8		
Beard (1996)	Broadcast/Tarp	Florida	36.5		
Rotonardo (2004)	Drip/low perm. tarp		15	11.8	27.2
Knuteson and Dolder (2000)	Drip/low perm. tarp	California	8.6		
van Wesenbeeck and Phillips (2000)	Drip/high perm.tarp	Georgia	12.3	12.3	-